

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Improvements relating to the Coating of Metallic Surfaces

We, THE PYRENE COMPANY LIMITED, a British Company, of Great West Road, Brentford, Middlesex, do hereby declare the invention, (a communication from Parker Rust Proof Company, a Corporation organised under the laws of the State of Michigan, United States of America, of 2177 East Milwaukee Avenue, Detroit 11, Michigan, United States of America) for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the formation of protective coatings on metallic surfaces by treating them with an aqueous composition which interacts with the surface.

Hitherto such compositions, which are generally solutions of coating-forming ingredients, have been applied either by flooding the surface with the aqueous composition, for example by immersion or roller coating, or by spraying the composition on the surface. Each of these methods is still widely used, and each has a field of operation in which it represents the most economical and most satisfactory method of application. However, each of these methods has drawbacks. Thus while flooding methods are highly satisfactory where heavy coatings are desired they are relatively slow, while the spray method is faster but is not particularly suited for use in the production of heavy coatings.

In both the spray and immersion methods the draining of the solution from the surface gives rise to problems. Firstly, the draining solution tends to flow in small rivulets and to form more or less coating in the path of flow than on the balance of the surface. Secondly, where the draining solution leaves the surface it tends to form a bead, beneath which the thickness of the coating again differs from that over the main part of the surface. These non-uniformities in the coating cause

difficulties both in painting and in otherwise using the coated surface.

Another problem which is common to both spray and immersion application methods is that the composition of the solution tends to change with continued use, and special steps have to be taken to maintain it at its optimum composition. For example, certain of the coating-forming chemicals in the coating solution may be used up faster than others; certain non-coating-forming ions may tend to increase to detrimental concentrations; the solution may undergo oxidation; and foreign ions may enter the solution from the surface being coated. Oxidation of a coating solution is particularly likely to occur when it is sprayed through the air.

These difficulties are overcome according to the invention by preheating the surface to be coated and applying the aqueous coating composition in the form of finely divided particles, the temperature of the surface and the size and quantity of the particles being so correlated that the particles dry substantially in the position where they first strike the surface. It should be noted that although the coating formed by the particles is dry, it may contain water of hydration. The conditions are preferably such that excess water is driven off substantially instantaneously on contact with the surface. By working in this way flow of the coating composition over the surface, and consequent formation of rivulets and beads, is avoided, and excess of the composition is not drained from the surface for re-use. Provided the particles are applied uniformly over the surface, the coating will also be uniform.

The thickness of the coating may be increased by applying further layers of the coating composition in the same way. At least the first layers of the coating will consist of or contain the products of interaction of the coating composition and the surface, but subsequent layers may consist wholly or largely of

solidified coating composition. In some cases these dried upper layers may include water-soluble components and a part of the coating may be removed by rinsing with water, and with certain combinations of metal and coating composition, the coating may be completely water-soluble. If necessary the coating is cured after application.

5 The process of the invention may be used  
10 to coat both bare metal surfaces and surfaces which already have an integral coating thereon. In the former case the coating composition must be capable of reacting with the metal itself, and in the latter case with the pre-  
15 formed integral coating on the metal. The metals that can be coated include all those that can be used to react with aqueous acidic or alkaline coating compositions, e.g. including  
20 iron, steel, zinc, copper, aluminium, magnesium, brass, bronze and stainless steel. Among the already-coated surfaces that may be further coated are phosphate-coated surfaces, which may for example be given a chromate  
25 rinse. Preheating a metal surface in air may also produce an adherent oxide film which may react with the coating composition.

30 The aqueous coating composition may be in any form which can be reduced to finely divided particles, but is preferably a dilute aqueous solution, dispersion or emulsion. In particular the coating composition may be an aqueous acidic coating-forming solution of zinc phosphates, manganese phosphates, iron phosphates, alkali metal phosphates, oxalic acid or  
35 oxalate, a mineral acid solution, an aqueous acidic solution containing ions capable of forming sulphide coatings, such as sulphide or sulphite ions, a dilute acidic rinse solution, e.g. a chromic acid or dichromate solution,  
40 with or without additional acids as modifying ingredients, used to rinse bare metal or previously chemically coated metallic surfaces, an amine phosphate coating solution, an acidic or alkaline metallic chromate solution to form  
45 finish coatings or rinse coatings over preliminarily formed metallic phosphate or similar coatings, or a dilute aqueous dispersion or emulsion of phosphate having lubricating properties, e.g. lauryl phosphate.

50 The present invention is particularly suitable for producing a chromium-containing coating on a bare or phosphate-coated metal surface by forming a film of an aqueous solution of a hexavalent chromium compound on the surface, the solutions also containing an  
55 organic polymeric or resinous material, and then drying the film on the surface, the organic material, which is preferably polyvinyl alcohol or polyacrylic acid, and the conditions  
60 of drying being such that an insoluble coating is formed. Coating compositions for forming such a chromium-containing coating are described in our Specifications Nos. 840,890 and 845,259.

65 A metal surface to be coated should be in

the condition conventionally used in coating by spraying or immersion; no further special cleaning is required.

The surface being coated must be hot enough both for reaction to take place between it and the coating composition and also for excess water and other volatile constituents to be rapidly vapourised. The exact temperature required will therefore depend among other factors upon the nature of the metal and of the coating composition. It is well known, for example, that the temperatures at which different phosphate-coating solutions operate most efficiently may vary as much as 100°F. In general it is found that metal being coated should be so heated that the surface temperature is at least 135°F after the coating composition has been applied, and it may be as high as 800°F. The metal should not, however, be heated to such a temperature that its metallurgical properties, e.g. hardness and elasticity, are impaired. Initial temperatures between 175°F and 500°F have been found in most cases to be satisfactory. Heat will be lost by the metal both in raising the temperature of the coating composition applied to it and in vaporising excess water and other volatile matter, so that the temperature of the metal will tend to fall during the coating process. If, as will generally be the case, all the heat needed is supplied by preheating the metal before applying the coating composition, the metal must therefore be preheated above the desired final temperature to an extent that will, under given coating conditions, depend on the thickness of the metal. Thus thin metal articles will need to be preheated to a higher initial temperature than thick ones in order to maintain a suitable surface temperature throughout the coating process.

Less heat will of course need to be supplied by the metal if the coating composition is also preheated above room temperature, and it may be advantageous, particularly when the metal is thin, to continue heating the metal, for example by means of infra-red lamps or by electrical induction, during the application of the coating composition.

It may also be desirable to supply further heat after the coating has been applied in order to complete the reaction with the metal surface, particularly when the coating is thick, or to cure the coating if it is a film-forming type containing synthetic resinous ingredients. This extra heat may for example be supplied by conventional ovens or by infra-red or radiant lamps.

The rate of vaporisation of water from the coating composition will depend on the humidity of the atmosphere which envelops the surface being coated as well as the temperature. It is therefore desirable to provide an exhaust system to remove the water vapour and other vaporised constituents from the neighbourhood of the surface. This may enable

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a lower temperature to be used. In no circumstances should the temperature in the neighbourhood of the surface be allowed to remain saturated with water vapour during the application of the coating, as this may slow down the evaporation of excess water so much that the particles are able to coalesce and run over the surface.

The aqueous coating composition is preferably converted to finely divided particles and applied to the surface by means of a suitable atomising gun, and both the size of the particles or droplets formed and the quantity of these particles applied to a given area of the surface to be coated must be correlated with the temperature of the metal to ensure that the particles do not have a chance to run before the excess water has evaporated. The particles may be applied over the whole surface by moving the atomising gun or other source of atomised particles relative to the surface or moving the surface relative to the source. The quantity of coating material per unit area of the surface being coated to obtain the most uniform coating depends both on the size of the particle and the speed of relative motion between the source of atomised particles and the surface to be coated. A uniform coating on the entire surface is most easily obtained when the particles are extremely fine and the relative motion is slow. Under these circumstances, as the minute particles hit the surface substantially all of them tend to remain in place, react with the underlying surface and lie immediately adjacent to each other without pyramiding to sufficient extent to become sufficiently liquid to flow during atomisation. As the particle size increases, in order to avoid coalescence sufficient to produce surface irregularities, it is necessary to increase the rate of relative motion between the source of the particles and the surface being coated. As this relative rate of motion is increased, however, it becomes increasingly difficult to obtain a uniform distribution of these larger size particles over the surface and ultimately to produce a coating having a uniform weight over the entire surface subjected to atomisation.

For different coating combinations it has been found that the particles in the coatings may vary from as small as 15 microns in diameter to as large as 350 microns in diameter and that most coatings comprise a mixture of particle sizes. When the particle sizes in the atomised coating material form particles in the coating within this range it is possible to regulate the temperatures of the substrate and the rate of relative motion between the source of the particles and the substrate being coated to obtain a uniform coating. It is even possible to prepare coatings useful for certain purposes when some of the particles in the coating exceed the size of 350 microns and range as high as about 500 microns in diameter, but

such coatings are usually less uniform and thus less desirable for most applications than the coatings including the above small range of particle sizes.

As a general guide to selecting the optimum operating conditions for the selected substrate and coating material it may be pointed out that for a given size of particle atomised toward the surface at a fixed rate, the resulting coating tends to increase in weight as the temperature is increased. At a given temperature and a fixed size of particle emanating from the atomising nozzle, an increase in the rate of relative motion between the atomising nozzle and the surface to be coated results in a lower coating weight and ultimately will produce non-uniformity in the coating. Under fixed conditions of temperature and relative motion between the atomising nozzle and the surface to be coated, increasing the particle size tends to increase the coating formed and ultimately results in coalescence or piling up of the particles or running of the applied coating or both. As a lower limit, the weight of coatings whose purpose is to improve corrosion resistance or enhance paint receptivity should be at least 7 to 10 mg./sq. ft. With chromic acid and chromate-containing solutions an improved result is obtained with coating weights lower than 7 mg./sq. ft. and even as low as 2 to 5 mg./sq. ft. particularly where the chromate-containing solution is applied as a rinse over integral chemical coatings. For the majority of the solutions of this invention such as the phosphates, oxalates, oxides, etc., it is preferred to form a coating weighing at least 20 to 50 mg./sq. ft. With these guides in mind it is relatively easy to arrive at the optimum conditions by a few simple tests under operating conditions.

In applying the coating composition care should be taken not to direct the particles at the surface at too high a velocity or at too acute an angle, as this may cause an appreciable proportion of them to bounce off the surface. It is also important that the surface should be substantially free of water at the moment of impact of the atomised particles of the coating composition. In the presence of a continuous film of water on the surface the discrete particles tend to slide or migrate on the surface rather than remain stationary in the position of impact, and this results in a non-uniform coating.

The coating compositions may be atomised by means of any conventional spray guns or nozzles that are capable of forming small enough particles. Both internal and external mixing types of spray guns may be used, with either suction or pressure feed of the composition into the propellant chamber. Relatively dilute solutions can satisfactorily be applied using suction feed spray guns, but somewhat better results are obtained from the use of pressure on the coating-forming solution as

well as on the propellant. Installations for coating large areas of continuously moving surface may include multiple jets arranged on suitably spaced headers.

5 Any readily compressible gas which does not liquefy or solidify at low pressures and does not produce undesirable side effects is satisfactory as a propellant. However, air and steam are preferred, because they are inexpensive, readily available and perform well. Superheated steam has been found to be an especially good propellant. It atomises well and because of its condensation on contact with cooler air it decreases the volume of the spray and thus prevents any toxic elements which might be present in the spray from drifting off into the surrounding air. It is therefore the preferred propellant when ventilation is a problem. Low quality steam should not be used, since the water content causes the condensation of its moisture on the metal surface during the spraying process.

As mentioned above, the coating may be built up to any desired thickness by repeated applications of the aqueous coating composition in the same way as has already been described, the metal being reheated if necessary between applications. The weight of the coating applied in any particular case will depend on the intended use. For example, a coating applied to impart corrosion resistance preferably has a weight in the range 150 to 450 mg./sq. ft. whereas a coating applied for wear resistance or lubricating purposes preferably has a weight in the range 750 to 2000 mg./sq. ft. Paint base coatings are generally lighter, for example 50 to 200 mg./sq. ft.

Since in working according to this invention a coating solution is used once only it is not necessary to provide a second replenishment solution of different composition.

The following Examples, which in no way limit the scope of the invention, illustrate the formation of various different types of coating according to the invention and the properties of the coatings obtained.

#### EXAMPLE I

A number of 4" x 6" panels of an aluminium alloy containing 1—2% magnesium were cleaned by immersion in a 3 oz./gallon aqueous solution of sodium pyrophosphate for five minutes, removed, rinsed and thereafter heated in air to a temperature of about 200°F.

An aqueous solution was prepared to contain:

	Grams
H <sub>3</sub> PO <sub>4</sub> (75%)	259
HNO <sub>3</sub> (42° Baumé)	290
ZnO	162
ZnSiF <sub>6</sub> .6H <sub>2</sub> O	50
Water to make 2000 ml.	

This liquid was placed in a suction feed type MBCL "DeVilbiss" atomizing gun (DeVilbiss catalogue I-2801) provided with a No. 32 LE nozzle and a 1115 ES liquid feed nozzle 0.070 inches in size, and atomised using a line pressure of 70 p.s.i.g. with the liquid nozzle opened one-fourth of a turn from its closed position. ("DeVilbiss" is a Registered Trade Mark). Several of the cleaned and heated aluminium panels were coated with the coating solution by holding the gun about 8 inches from the panel surface and moving the nozzle across the panel surface at a speed of about 50 feet/minute, after which the panel was reheated with infra-red lamps to about 200°F. and coated with an additional similar pass. The panels were then cured for 3 minutes by heating in an air atmosphere furnace at 450°F. The complete coating weighed about 600 mg./sq. ft. Upon inspection the coatings were found to be uniformly distributed, hard, and light grey in colour. The coatings were insoluble in boiling hot water.

Three additional solutions were then prepared by modifying the above composition to contain 100, 150 and 300 grams of ZnSiF<sub>6</sub>.6H<sub>2</sub>O respectively.

Further similar aluminium panels were coated with these solutions, using identical conditions to those described above. Upon inspection after curing all were found to have on their surfaces adherent coatings. As the quantity of ZnSiF<sub>6</sub>.6H<sub>2</sub>O increased, the dullness of the light grey coating became more and more pronounced. The panels treated with the solution containing 150 grams ZnSiF<sub>6</sub>.6H<sub>2</sub>O had the most uniform coatings. In all other respects the panels were comparable.

#### EXAMPLE II

A solution of the following composition was prepared:

	Grams
H <sub>3</sub> PO <sub>4</sub> (75%)	259
HNO <sub>3</sub> (42° Baumé)	290
ZnO	162
ZnSiF <sub>6</sub> .6H <sub>2</sub> O	200
ZnF <sub>2</sub>	100
Water to make 2000 ml.	

Aluminium panels were prepared and coated with this solution as described in Example I. The coatings produced were similar in dullness to those resulting from the coating solution containing 300 grams ZnSiF<sub>6</sub>.6H<sub>2</sub>O and slightly smoother but in other respects substantially the same.

#### EXAMPLE III

An aqueous solution was prepared to contain:



particle size and coating weight which result from alterations in the atomizing conditions of application. Several 4' x 6' panels of low carbon steel were cleaned by conventional methods and then preheated to a temperature in the range of about 350°F. to about 400°F. An aqueous admixture was prepared containing 2% CrO<sub>3</sub> and 1% polyacrylic acid. This aqueous admixture was placed in a "DeVilbiss"-type AGA spray gun using nozzle G and a 763 air cap, the liquid aperture in the nozzle being 0.026" diameter. This equipment is described in detail in DeVilbiss catalogue IE—E, and is a spray gun using pressure on the aqueous admixture in the tank and a separate source of gaseous propellant. The pressure employed on the propellant, air, was 60 psig., and the pressure in the tank was 20 psig. With the rate of relative motion between the spray gun and the panels of approximately 60 feet/minute a single pass over the surface produced on the panels a coating weight in the range of 2 to 5 mg./sq. ft. The coatings were cured by heating the panels in an oven at a temperature of 375°F. for about 3 minutes and then withdrawing them. An inspection of the coated surface showed irregular coated areas separated by uncoated areas.

Another set of similarly cleaned panels were atomization coated in the same way with the same solution, the pressure on the chromic acid-polyacrylic acid admixture being increased to 25 psig. The cured coatings which resulted from a single pass of the atomizing gun over the surface at the same speed weighed between 5 and 10 mg./sq. ft.

Another set of similar panels was atomization coated in the same way with the same admixture, the pressure on the admixture being increased to 40 psig. After one pass over the surface at the same relative speed, and curing, an inspection of the surface showed a coating having a weight in the range 10 to 15 mg./sq. ft., but in this case the coating was interspersed with globules of coating, some of which were as large as about 1 mm. in diameter.

All three sets of coated panels were painted with a white primer coat and a white enamel finish coat and were tested for corrosion resistance by spraying with a 20% sodium chloride solution. After 312 hours in the salt spray chamber the panels resulting from the use of 20 psig. pressure on the coating admixture were found to be only about one-half as resistant to corrosion as those panels resulting from the use of 25 and 40 psig. pressure on the coating admixture.

The particle size of the particles resulting from use of the 20 and 25 psig. pressures on the liquid admixture was approximately the same but with the lower pressure the rate of flow of the coating admixture relative to the

rate of traverse of the surface was insufficient to produce a quantity of coating to provide the desired surface protection. By increasing the pressure on the coating material to 25 psig. and maintaining the air propellant pressure of 60 psig. the coating weight was increased to 5—10 mg./sq. ft., which was a sufficient quantity of material to provide the desired surface protection. When the pressure on the chromic acid-polyacrylic acid admixture was increased to 40 psig. however, the particles which resulted were irregular in size and much larger and the resulting coating included the non-uniformity spaced globular particles.

On increasing the pressure on the air propellant to 80 psig. while maintaining the pressure on the chromic acid-polyacrylic acid admixture at 40 psig. uniformly sized particles were again produced which, upon spraying similar panels under similar conditions gave a uniform coating having a weight of about 20 mg./sq. ft. When these panels were painted in a comparable fashion and tested for corrosion resistance they were found to be even better in corrosion resistance than the panels containing 5—10 mg./sq. ft.

#### EXAMPLE VIII

A group of zinc coated steel panels 4" x 6" x 1/16" was heated to 160°F. and another group of comparable panels was heated to 450°F. Two aqueous compositions were prepared, one of which contained 2% chromic acid and 2% polyacrylic acid weight/volume, and the other of which contained 2% polyacrylic acid and 4% chromic acid, weight/volume. Each of these aqueous admixtures was placed in an MBCL spray gun having a 32 LE nozzle, 0.070" liquid feed nozzle diameter, (DeVilbiss catalogue I—2801) and the panels were coated by employing an air propellant pressure of 60 psig. and a rate of flow of the admixture of about 1 quart/hour. Under these conditions the spray particles had a size in the range 3 to 25 microns and after curing the coatings by positioning the panels for about 3 minutes in an oven at 375°F., the coatings were found to have a typical metallic appearance, slightly glossy and to be uniformly distributed over the surface. The coatings were hard, had a weight in the range 18 to 36 mg./sq. ft. and were insoluble in boiling hot water. These panels were tested for humidity resistance by subjecting them to a humid atmosphere for one week, and upon inspection they were all found to be substantially free from white corrosion products.

#### EXAMPLE IX

Another set of 4" x 6" aluminium panels were prepared for coating as set forth in Example I. The following aqueous solutions were compounded:





5 This solution was found to have a total acid of 10.3. A number of these panels were coated under the conditions specified in Example VI, and on inspection were found to be coated with a grey adherent phosphate coating of typical appearance.

#### EXAMPLE XIV

10 4" x 6" cold rolled steel panels were solvent cleaned and coated by conventional spray application of an aqueous solution containing zinc 0.14%, PO<sub>4</sub> 0.75%, nitrate (NO<sub>3</sub>) 1.8%, all percentages being weight per volume. The solution had a free acid of 0.7 and a total acid of 10.1. With the solution at a temperature of 135°F. the panels were spray flooded with the solution for a one minute period of contact to produce coatings having an average weight of about 265 mg./sq. ft. These panels were preheated to a temperature in the range 20 175—200°F. in an air atmosphere furnace maintained at a temperature of about 300°F. Groups of these heated phosphate coated

panels were then atomization coated with various hexavalent chromium-containing rinse solutions by employing the atomization equipment identified in Example I. After application of the rinse solutions certain of the panels were cured by positioning them in a furnace at 300°F. for 30 seconds and withdrawing while others of the panels were positioned for 3 minutes in the same furnace prior to withdrawal. The thus coated panels were tested for salt spray resistance in comparison with panels of the same steel which were uncoated and which were similarly phosphate coated and rinsed in a conventional chromic acid liquid solution in the current commercial manner. Other panels were painted with a primer and a finish white enamel and these panels were scratched diagonally from corner to corner to form an X on the painted surface and tested for salt spray resistance as well as humidity. The relative results of these tests are summarized in Table I.



TABLE I

Test No.	Atomization Rinse Percent by Wt.	Curing	Ctg. Wt. Mg./ft. <sup>2</sup>	Hours in Salt Spray							Hrs. in Humidity				
				Bare Coating				Painted			Painted				
				2	3	4	5	7	144	288	504	144	312	504	
1	.1CrO <sub>3</sub> —.1H <sub>3</sub> PO <sub>4</sub>	Air Dried	16	3L	4ML	5ML	5M	—	—	0	0	0	0	B <sub>1</sub>	B <sub>1</sub>
2	.05CrO <sub>3</sub> —.05H <sub>3</sub> PO <sub>4</sub>	Air Dried	8	5L	5ML	5ML	5M	—	—	0	0	0	B <sub>1</sub>	B <sub>2</sub>	B <sub>2</sub>
3	.1CrO <sub>3</sub>	Air Dried	5	5L	5M	—	—	—	—	0	0	0	0	B <sub>1</sub>	B <sub>1</sub>
4	Sol. I—.05CrO <sub>3</sub>	30 seconds at 300° F.	5	5M	—	—	—	—	—	0—1	0—1	1—3	0	0	B <sub>1</sub>
5	Sol. I—.5CrO <sub>3</sub>	30 seconds at 300° F.	50	1L	4L	5ML	5ML	5M	5M	0	0	0	B <sub>1</sub>	B <sub>1</sub>	B <sub>1</sub>
6	Sol. II—.05CrO <sub>3</sub>	3 minutes at 300° F.	4	5ML	5ML	5M	—	—	—	1—1	2—3	3—7	0	0	0
7	Sol. III—.05CrO <sub>3</sub>	3 minutes at 300° F.	4	5M	5M	—	—	—	—	0	0—1	0—1	0	0	B <sub>1</sub>
8	Sol. I—.5CrO <sub>3</sub>	3 minutes at 300° F.	50	0	1.5L	1.5L	2L	4L	—	0	0	0	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>
9	Bare Controls	—	—	5M	—	—	—	—	—	1—1	2—3	4—9	0	0	B <sub>1</sub>
10	.01CrO <sub>3</sub> —.015H <sub>3</sub> PO <sub>4</sub>	3 minutes at 300° F.	Control	5M	—	—	—	—	—	1—1	2—3	4—7	B <sub>1</sub>	B <sub>1</sub>	B <sub>1</sub>
I—3% CrO <sub>3</sub> , 1.5% Polyacrylic acid (25%), 1.8% PO <sub>4</sub> as Zn (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O															
II—4% CrO <sub>3</sub> , 2% Polyacrylic acid (25%), 1% PO <sub>4</sub> as Zn (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O															
III—3% CrO <sub>3</sub> , 1.8% PO <sub>4</sub> as Zn (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O (In each case, solutions I, II and III were diluted to produce the CrO <sub>3</sub> concentration shown)															

- In Tables I, II and III, the salt spray resistance, bare coating, is reported on the basis of the proportion of the surface coated with rust ranging between 1 and 5, 1 being a small portion of the surface and 5 being the total surface. L is light rust, VL is very light rust and M is medium rust so that, for example, 5 M means that the panel is entirely coated with medium rust. The salt spray resistance of the painted panels is reported on the basis of the number of sixteenths of an inch which rust had proceeded from the scratch marks diagonally across the panel. Zero means no rusting, 0—1 means rust has proceeded a maximum of one-sixteenth of an inch and a minimum of zero, whereas 4—9 means that the rust has migrated a maximum distance of nine-sixteenths of an inch and a minimum of four-sixteenths along the diagonals. Humidity is reported on the basis that A indicates bottom edge blistering and B indicates surface blistering while the subscripts vary between 1 and 5 and B<sub>s</sub> indicates severe blistering over the entire surface.
- On this comparative basis it can be seen that tests 1, 2 and 3 all gave better bare coating resistance in salt spray than the controls. Excellent spray and humidity results were obtained, bare and painted, in tests 5 and 8 in which the coating weights are extremely heavy relative to coating weights obtainable with normally employed aqueous solution rinsing techniques. In each of these cases there was no rundown and no problem of chromic acid build-up at the draining edges of the panels as is characteristic of normally rinsed parts.

## EXAMPLE XV

A large number of 4" x 6" cold rolled steel panels were solvent cleaned, degreased and rag wiped and then immersed in an aqueous solution containing 0.4% Zn, 1.6% PO<sub>4</sub>, 1% NO<sub>3</sub>, and 0.2% ferrous ion, the solution having a total acidity of 30.2 (total acidity of 10 ml sample titrated to phenolphthalein endpoint with N/10 sodium hydroxide). This solution was heated to 185°F. and the panels immersed therein for 30 minutes and withdrawn. This resulted in the formation of a zinc phosphate coating having an average weight of 1000 to 1500 mg./sq. ft. These coated panels were then heated in an air atmosphere furnace at 300°F. for approximately 20 seconds to raise their temperature to 175 to 200°F. The panels were then atomization coated using the apparatus of Example II and the general procedure there described, except that the rinse solutions were modified in composition and the thickness of the dried solutions varied as set forth below in Table II, which shows the comparative results of salt spray tests on the panels. Certain of the panels, after atomization coating but before subjected to salt spray testing, were oiled by dipping the coated panels in a commercial oiling composition comprising zinc stearate thinned with mineral spirits, removing them and allowing them to dry. Control tests for salt spray resistance were carried out on identical bare panels and on panels which received similar phosphate coating and typical commercial rinsing in an aqueous dilute hexavalent chromium rinse solution containing about 0.01% CrO<sub>3</sub> and 0.015% H<sub>3</sub>PO<sub>4</sub>.

TABLE II

Test No.	Atomization Rinse Percent by Wt.	Curing	Ctg. Wt. Mg./ft. <sup>2</sup>	Hours in Salt Spray											
				Dry						Oiled					
				2	4	6	10	14	20	26	24	48	118	190	
1	.5CrO <sub>3</sub> —.5H <sub>3</sub> PO <sub>4</sub>	Air Dried	75	0	0	3L	5L	5L	2	4	0	0	2	3.5	
2	1CrO <sub>3</sub> —1.5H <sub>3</sub> PO <sub>4</sub>	Air Dried	150	0	0	0	0	1	2	3	0	0	1	2	
3	1%CrO <sub>3</sub>	Air Dried	50	0	0	0	2L	1	3	4	2	2	3	4	
4	Sol. I—.5CrO <sub>3</sub>	30 seconds at 300° F.	35	5VL	5L	5L	5L	5L	2	3	1	1	1.5	5	
5	Sol. II—.5CrO <sub>3</sub>	"	35	4VL	5L	5L	5L	5L	5ML	5	1	1	1	3	
6	Sol. III—.5CrO <sub>3</sub>	"	50	4VL	5L	5L	5L	5	—	—	0	1	1.5	3	
7	Sol. IV—.5CrO <sub>3</sub>	"	35	2VL	5VL	4	5	—	—	—	2	2	3.5	5	
8	Sol. V—.5CrO <sub>3</sub>	"	40	4VL	5VL	5VL	5	—	—	—	0	0	2.5	5	
9	Sol. I—.5CrO <sub>3</sub>	3 minutes at 300° F.	35	0	0	0	0	1	2	3	0	0	5L	5	



By inspecting Table II it may be seen that the air dried rinses of tests 1, 2 and 3 showed considerable improvement in salt spray resistance relative to the controls and test 2 is outstanding in corrosion resistance, the  $\text{CrO}_3$  coating being 150 mg./sq. ft. Tests 4 to 13 showed that all of the samples were substantially better than the controls, in both dry and oiled form where 30 seconds and 3 minutes were used for curing the coating.

#### EXAMPLE XVI

A large number of 4" x " cold rolled steel panels were solvent cleaned, degreased and rag wiped and then immersed in an aqueous solution containing 3.75%  $\text{PO}_4$ , 0.04% Ni, 0.56% Mn, 0.2%  $\text{NO}_3$  and 1.8%  $\text{Fe}^{++}$  and having a free acid of 2.0 and a total acid of

12.0 (2 ml sample titrated to phenolphthalein endpoint with N/10 sodium hydroxide). The cleaned panels were immersed in the solution at 200°F., allowed to remain therein for 15 minutes and withdrawn, after which they were found to be coated with an average coating weight between about 900 and 1200 mg./sq. ft. All of the panels were atomization coated with various hexavalent chromium-containing solutions. Certain of the panels were oiled and all were tested for resistance to corrosion in a 20% sodium chloride salt spray for various times, relative to both bare controls and phosphate coated controls conventionally rinsed in a solution containing .01%  $\text{CrO}_3$  and .015%  $\text{H}_3\text{PO}_4$ . The results of these tests are summarized in Table III.



An inspection of this Table shows substantial improvement in salt spray resistance both dry and oiled for light and heavy weight coatings relative to the controls.

# 5 EXAMPLE XVII

Lubricating and corrosion-resistant coatings were formed by atomization spraying on mild steel panels having a temperature of about 250°F. one of the following dispersions: 10 monolauryl phosphate—160 grams; morpholine—32 grams; zinc acetate—25 grams; sodium chlorate—35 grams; 0.4% sodium meta-nitro benzene sulphonate; each mixed with distilled water to make 2 gallons. The 15 equipment and the basic procedure described in Example 1 were used. The coatings formed were uniformly distributed and crushed to an unctuous film upon the application of pressure.

## WHAT WE CLAIM IS:—

20 1. A process for forming a protective coating on a metallic surface by treatment with an aqueous coating composition which interacts with the surface or with an integral coating thereon which comprises preheating the surface 25 and applying the coating composition in the form of finely divided particles, the temperature of the surface and the size and quantity of the particles being so correlated that the particles dry substantially in the position 30 where they first strike the surface.

2. A process according to claim 1 in which the temperature of the surface is maintained at at least 135°F during the application of the coating composition.

35 3. A process according to claim 1 or claim 2 in which the surface is preheated to a temperature of 175—800°F before the application of the coating composition.

40 4. A process according to any of claims 1 to 3 in which the temperature of the surface is such that when the particles strike the surface the interaction between the coating composition and the surface and the drying of the particles are substantially instantaneous.

45 5. A process according to any of claims 1 to 3 in which further heat is supplied to the surface during the application of the coating.

50 6. A process according to any of claims 1 to 5 in which the coated surface is further heated after the coating has been applied in order to cure the coating.

7. A process according to any of claims 1 to 6 in which the thickness of the coating is

increased by further applications of the coating composition in the same manner.

8. A process according to any of the preceding claims in which the aqueous coating composition is applied in the form of particles having a size in the range 15—350 microns.

9. A process according to any of the preceding claims in which the finely divided particles are formed and applied to the surface by atomising the aqueous coating composition with a gaseous propellant.

10. A process according to claim 9 in which the surface is progressively coated by moving it relative to the source of atomised particles.

11. A process according to any of the preceding claims in which volatile material is continuously removed from the neighbourhood of the surface being coated.

12. A process according to any of the preceding claims in which the aqueous coating composition is an aqueous acidic phosphate solution.

13. A process according to any of claims 1 to 11 in which the aqueous coating composition is an aqueous acidic solution containing hexavalent chromium.

14. A process according to claim 13 in which the aqueous coating composition also contains an organic polymeric or resinous film-forming ingredient.

15. A process according to claim 14 in which the film-forming ingredient is polyvinyl alcohol or polyacrylic acid.

16. A process for improving the corrosion resistance of a metallic surface which comprises forming a phosphate coating on it and subsequently coating it in accordance with any of claims 13 to 15.

17. A process according to claim 1 substantially as described in any of Examples I to XVII.

18. A metallic article having on its surface an adherent integral coating produced by the process of any of claims 1 to 15.

19. A metallic article having on its surface a phosphate coating and an overlayer of a material containing hexavalent chromium produced by the process of claim 16.

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